Appendix D

Microgravity Effects on Materials Processing: A Review

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ABSTRACT

Materials processing in space has been studied both theoretically and experimentally for over ¼ of a century. In the beginning, we naively spoke of "zero gravity," elimination of convection, growth of perfect crystals, and eventual manufacturing in space. All of these appear to have fallen by the wayside. On the other hand, we have learned an unprecedented amount about the influences of gravity on materials processing. We have had many surprises, and not all experimental results have yet been satisfactorily explained. Gravity was found to influence processes that were thought to be gravity-independent. One consequence is that materials processing on earth has often been improved. And it is difficult to imagine how the materials-processing industries could have flourished without the engineers and scientists who received their training by working on microgravity materials processing.

KEYWORDS: Microgravity, solidification, convection, eutectics

INTRODUCTION

This review is necessarily limited in scope and depth, both because of the page limit for these proceedings and because the amount of published literature on microgravity materials processing is now enormous. Consequently, the topics emphasized are those of particular interest to the authors. We apologize to those whose work or publications were not described or cited. Much information is now available on the web [1].

The dreams of manufacturing "perfect" crystals using "zero gravity" began in the 1960's during the Apollo era. Talk of manufacturing other substances continued through the 1970's and much of the 1980's. Then reality set in, particularly with the Challenger disaster. The space environment was not magic and the materials were not sufficiently better to warrant the costs. The value added did not exceed the additional cost. On the other hand, an immense amount was learned about gravitational effects on materials process, both through the results of space experiments and through related ground-based research. In fact, many results were unanticipated and some await full explanation. This knowledge has proven to be extremely useful in improvement and innovation of materials processing on earth.

When the dream of manufacturing in space began in the 1960's, a major problem in semiconductor device manufacturing was variation in impurity doping, on both macroscopic and microscopic scales. Semiconductor crystals were grown by Czochralski crystal pulling and by Bridgman techniques.[1] In Czochralski growth, periodic variations in impurity concentration arose from the

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[1] In Czochralski growth, a vertical crystal is slowly pulled from a melt contained in a crucible. Usually, both the crystal and the crucible are rotated in order to produce a cylindrical crystal. In Bridgman growth, directional solidification

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rotation of the crystal while it was being pulled from the melt. The resulting bands were known as "rotational striations," with the distance between them equal to the amount grown in one rotation. More closely spaced striations in both Czochralski and Bridgman-grown crystals arose from buoyancy-driven convection. In addition to the striations, convection in the melt led to a long range variation in impurity concentration down the length of the crystal. Bridgman growth in space seemed to offer the perfect solution to this problem -- utilizing zero gravity to eliminate convection, and, thereby, to give a constant impurity concentration.

Subsequently, both experimental measurements and theoretical estimates showed that the acceleration is not zero in an orbiting spacecraft. The steady acceleration level was estimated to be on the order of one-millionth of earth's gravity. Thus, the term "zero gravity" died and "microgravity" was born. The estimates of steady acceleration accounted for the separation from the center of mass of the spacecraft, rotation of the spacecraft, and atmospheric drag. Measurements showed considerably larger fluctuating accelerations, averaging approximately one-thousandth of earth's gravity. These were often termed "g jitter," and arose from movements of the crew, operation of equipment, spacecraft attitude adjustment, and waste dumps.

The residual acceleration in spacecraft always causes buoyancy-driven convection. Theoretical estimates were performed that were based on a steady or varying body-force term in the Navier-Stokes equations of motion [e.g.,2,3,4,5,6,7,8,9,10,11,12]. (This approach is really only appropriate for steady and low-frequency accelerations applied to a single-phase fluid in a rigid container.) It was concluded that convection should result, that the amount of convection increases with increasing acceleration and decreasing frequency, and that it will significantly influence some materials processing operations. The influence of flexible container walls and two-phase systems was not considered. It was shown both theoretically and experimentally that high-frequency vibration can cause significant "vibro convection" and can apply a force to second-phase particles [e.g.,13,14,15,16,17].

In recent years, it has become increasingly recognized that some microgravity experiments require reduced acceleration levels in order to be fully successful. Consequently, both passive and active vibration-damping systems have been devised. The most extensively tested active system is the Canadian Microgravity Isolation Mount (MIM) [18]. For example, the apparent diffusion coefficients[2] of liquids were much smaller values when measured on Mir and in the Shuttle than on earth, with still lower values when measured in MIM with active dampening [19,20,21]. G-jitter also affected Brownian motion of small particles, dynamics of a fluid-fluid interface, the distribution of nuclei in a glass, directional solidification of InSb, and bubble motion [20].

Another source of convection arises from a variation in surface tension along a fluid-fluid interface, due either to a variation in temperature or composition. The surface moves from the region with a low surface tension to that with a high surface tension, dragging the nearby fluid with it by viscous forces. This phenomenon has become known as "Marangoni convection." Prior to the space program, it had been ignored in investigations of materials processing on earth. In microgravity, the reduced level of buoyancy-driven convection allowed Marangoni convection to become obvious. We learned that this surface-tension-driven convection could not only be vigorous, but could also become oscillatory and even turbulent. It also leads to the movement and coalescence of drops and bubbles [22]. Once it became recognized, it was found to be significant in some earth-based processes as well.

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occurs within a vertical ampoule or a horizontal boat. The ampoule or boat is inside a furnace with a temperature that varies from above the melting point at one end to below the melting point at the other end. Freezing is caused by moving the ampoule through a fixed furnace or vice versa, or by slowly lowering the furnace temperature with both ampoule and furnace immobile. This latter method is often called the "gradient-freeze technique."

[2] Even a small amount of convection increases mass transfer and, thereby, the apparent diffusion coefficient.

Microgravity also greatly reduces sedimentation of second-phase particles, drops or bubbles in a liquid. The reduced hydrostatic head makes it much easier to nucleate gas bubbles in a liquid containing dissolved gas. Thus is it not surprising that more gas bubbles are often found in solids produced in space.

We see that the microgravity environment proved to be much more complex that envisaged 20 to 30 years ago. We now discuss some of the materials processing operations that are influenced by this environment. Again, we do not claim to be comprehensive.

DIRECTIONAL SOLIDIFICATION OF SEMICONDUCTORS

As mentioned earlier, the original motivation for Bridgman growth in space was to produce semiconductor crystals with completely uniform doping. Homogeneous crystals were sometimes produced in flight experiments, but only when the freezing rate was much greater than the convective velocity of the nearby melt. In fact theory indicates that there is a range of operating conditions where cross-sectional variations in composition are actually increased in microgravity. Reduced gravity was much more successful at eliminating compositional striations than at avoiding radial or macroscopic longitudinal variations.

Completely unexpected were results from Skylab in 1974 in which the crystal had a slightly smaller diameter than the ampoule. Similar results were often obtained in subsequent microgravity experiments, as reviewed in [23]. Sometimes miniature "walls of China" meandered across the surface and connected the crystal with the ampoule. Other times the separation was wide and the crystal surface was wavy. This phenomenon remained mysterious for 20 years until it was explained by the Moving Meniscus Model of Detached Solidification [24,25,26,27,28]. As shown in Figure 1, there is a gap between the crystal and the ampoule wall, while the melt is in intimate contact with the wall. A meniscus connects the edge of the growing crystal with the ampoule wall. A gas at pressure P_C fills the gap. This gas first dissolves in the melt at the end of the melt column at pressure P_H. Its solubility in the solid is much less than in the melt, so it is segregated out and concentrates in the melt at the freezing interface. From there, it diffuses into the gap through the meniscus. Detachment is favored by a high residual gas pressure P_H, high solubility of the gas in the melt, high contact angle ?, high growth angle ?, low melt-gas surface tension, and moderate growth rate. During growth, the meniscus moves along the surface of the ampoule wall at the freezing rate. This is the origin of the name for the model.
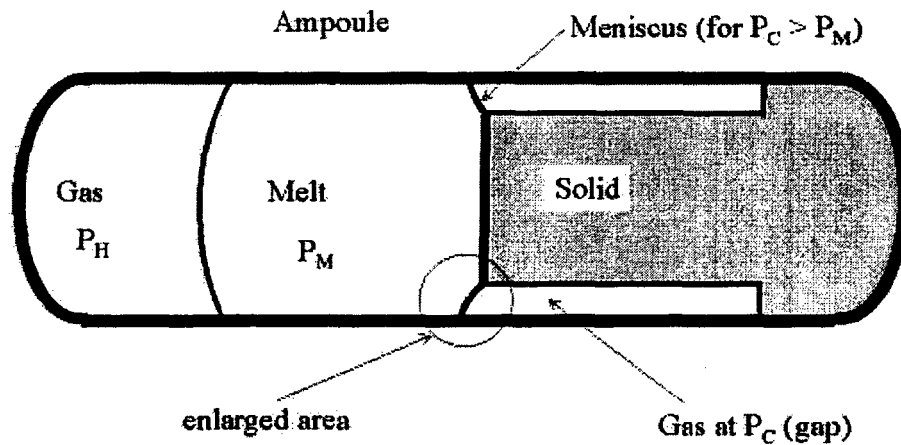
Figure 1. The Moving Meniscus Model of detached solidification [24-28].
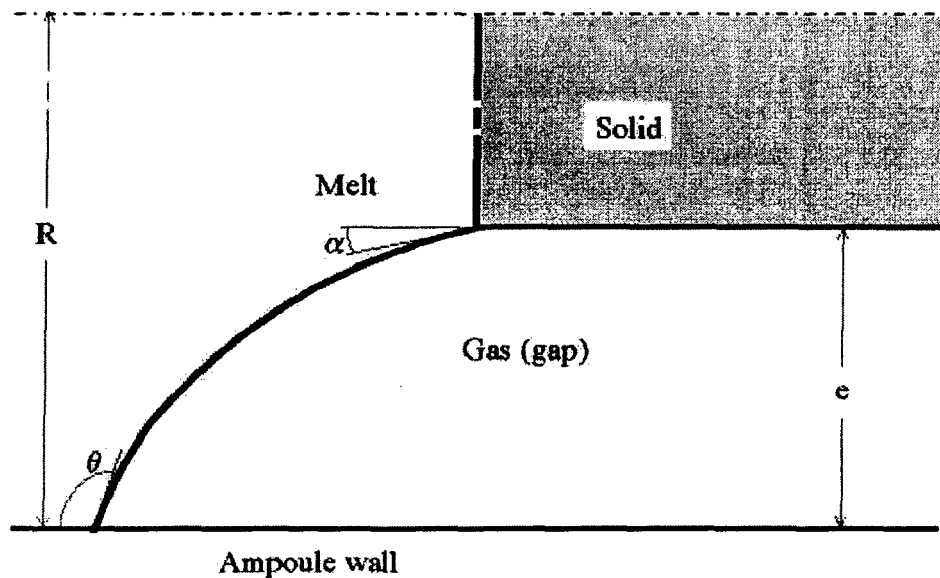The enlarged area is shown in Figure 2.

Figure 2. Enlarged meniscus area from Figure 1.

When detachment occurs during solidification, the crystallographic perfection is greatly increased. Without the solid adhering to the ampoule wall, the stress produced by differential thermal contraction is eliminated and dislocation generation nearly ceases. Without the growth interface contacting the ampoule wall, grain and twin generation nearly ceases. For these reasons, attempts are underway to produce detached solidification on earth. It has occasionally occurred serendipitously on earth, but until the Moving Meniscus Model was not understood. The only

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reported instance in which the meniscus and separated solid were observed *in situ* was with germanium in ground-based experiments performed in a mirror furnace [29]. The reason detachment has not been seen more often is that directional solidification has been performed in opaque furnaces at high temperature, so that it has not been possible to view the freezing material.

FLOATING ZONE MELTING

In floating zone melting, a molten zone is slowly moved through a vertical rod without a container. This enables crystals to be grown without contamination by the container material, with outgassing of volatile impurities, without stress due to sticking to an ampoule wall and differential thermal expansion, and without generation of grains and twins at a container wall. If one relies on surface tension to support the molten zone and the zone is approximately cylindrical, then the maximum diameter before the zone falls in earth's gravity is only a few mm. Thus it was proposed in the early "zero gravity" days that float zoning in space could yield large, high quality crystals with uniform doping due to the lack of convection. However, much larger crystals of silicon were already being grown commercially on earth by use of induction heating, with an hour-glass shaped melt that passed through a coil smaller in diameter than the crystal [30]. The electromagnetic field provides a levitating force, so that the melt tends to fall if power is lost. This same technique is applicable to materials that are electrically conductive and without volatile constituents. For other materials, it is expected that larger diameters can be float zoned in space than on earth. The suggestion that no convection would occur in the molten zone led to a theoretical investigation of Marangoni convection [31,32,33,34]. This investigation indicated that convection in silicon could be so vigorous that it would likely be oscillatory or even turbulent. Subsequent experimental and theoretical treatments by many investigators confirmed these predictions.

EUTECTIC SOLIDIFICATION

Generally speaking, eutectic alloys that freeze with a lamellar structure showed negligible influence of microgravity compared to directional solidification on earth. On the other hand, flight experiments on eutectics that yield fibers or rods often produced unexpected results that have been difficult to explain (reviewed in [35,36]). In some materials the fibers were closer together when solidification took place in microgravity, while in other alloys they were farther apart. These results were attributed to convection on earth perturbing the composition field near the freezing interface. However, theoretical analyses predicted that buoyancy-driven convection should have negligible influence on eutectic microstructure if the bulk composition and the average interfacial composition are both at the eutectic. The reason is that the concentration field extends out into the melt from the freezing interface an extremely short distance, on the order of the fiber spacing ?, so that it is insensitive to convection. It was also predicted that reduced convection should always cause the fibers to be closer together.

Because of the foregoing, it was suggested that buoyancy-driven convection on earth causes a fluctuating freezing rate that makes the microstructure differ from that with a constant freezing rate equal to the average of the fluctuating rate. This arises because the kinetics of fiber termination differs from that for fiber branching or nucleation. Recently, experiments were completed on the influence of electric current pulses during solidification on the microstructure of the MnBi-Bi eutectic [37]. Current pulses cause an oscillatory freezing rate whose amplitude and frequency can be controlled. For freezing rates over 2 cm/hr, current pulsing transformed sections of the ingot from a quasi-regular microstructure to irregular MnBi, broken lamellae or completely void of MnBi. The reverse was true at 1.1 cm/hr. For the quasi-regular portions, the average MnBi rod spacing decreased almost linearly with the average current. This result contradicts the hypothesis

that freezing rate fluctuations were responsible for the effect of convection on MnBi-Bi microstructure.

Another possible explanation for the influence of microgravity on microstructure points out that the average interfacial melt composition may not be at the eutectic during steady solidification [38]. Theoretical treatments also indicated that freezing rate fluctuations can alter the average interfacial composition in the absence of convection [39,40,41]. When the average interfacial composition deviates significantly from the eutectic, the region of concentration variation extends orders of magnitude farther into the melt from the freezing interface, causing it to become much more sensitive to convection.

Microgravity experiments on off-eutectic Al-Si alloy showed a finer eutectic microstructure between the arms, especially at lower freezing rates [42]. This was attributed to "microconvection" occurring between the phases on earth.

DENDRITIC GROWTH

Microgravity experiments using a single succinonitrile dendrite revealed that the growth velocity and tip radius are influenced by buoyancy-driven convection, especially when the supercooling is low [43,44]. These experiments were used to obtain data at low freezing rates in order to compare with theoretical predictions.

Solidification with a dendritic front and mushy zone has also been studied. The growth front of ammonium chloride dendrites growing from an aqueous solution advanced at about twice the rate in microgravity as on earth [45,46]. The mushy zone was more transparent in microgravity.

SOLIDIFICATION WITH IMMISCIBLE PHASES

In the early "zero gravity" days, it was suggested that it should be possible to easily solidify materials containing uniform dispersions of second-phase gas bubbles, liquid drops, or solid particles, because of the absence of sedimentation. Included were monotectic and peritectic systems where the second phase tends to separate by sedimentation on earth. Although microgravity sometimes yielded improvements in such dispersions [47,48,49], this was usually not true. Sometimes greater phase separation occurred in microgravity than on earth. Failure to obtain uniform dispersions was attributed to sedimentation due to the residual accelerations, surface-tension driven "Marangoni" motion of the drops or bubbles, lack of wetting of particles by the melt, and pushing of the second phase by the freezing interface [50,51,52,53,54,55,56,57]. For example, moving gas bubbles were thought to have perturbed the distribution of solid particles [58].

The presence of $FeAl_3$ particles assisted in producing a uniform dispersion of In droplets in the Al-In system both on earth and in microgravity, although the amount required was less in microgravity [59].

OTHER MATERIALS PROCESSING OPERATIONS

Time and space limitations prevent us from covering other materials processing operations. Suffice it to say that experiments have shown that microgravity influences polymerization, physical and chemical vapor transport, electrodeposition, coagulation (agglomeration) of large colloidal particles, Ostwald ripening, and self-assembly of nano-systems.

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ACKNOWLEDGEMENT

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